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Electron tunneling microscopy: a direct probe of metal substitution in BiSrCaCuO superconductors¹

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Abstract

Scanning tunneling microscopy (STM) exploits the extreme distance sensitivity of electron tunneling to achieve atomic resolution imaging of surfaces. The ability of STM to probe directly materials on the atomic scale has been exploited to elucidate the structural effects of metal substitution in the copper oxide superconductor Bi₂Sr₂CuO₆. A series of Bi₂Sr₂CuO₆ single crystals containing lead substituted in the bismuth-oxide layer have been prepared, and the structures of these materials have been characterized by STM. The measurements show that lead-substitution induces complex changes in the structural order of the parent compound. Comparisons of these data with electron diffraction measurements highlight the importance of local crystallography, which STM provides, in studying the chemistry of inorganic materials.

Keywords: Electron tunneling microscopy; Copper oxide superconductor

1. Introduction

Understanding the relationship between atomic level structure and observable properties of materials represents an important goal of solid state chemistry [1,2]. Chemical approaches to achieving this goal necessarily involve elucidating how material properties are determined by variations in the composition and structure of a solid. In principle, this information is readily available from diffraction measurements when solids exhibit highly ordered, crystalline structures. However, some of the most fascinating inorganic materials known today, such as the high-temperature superconductors, are not well-ordered [2,3]. These complex materials exhibit structural complexities such as substitutional disorder that conventional diffraction measurements cannot resolve, although such information is essential to understanding the chemistry and properties of these materials.

An experimental technique that can probe material properties directly on the atomic scale is scanning tunneling microscopy (STM) [2,4,5–10]. The underlying basis

for STM is similar to electron transfer reactions in molecular systems; that is, electron tunneling. In the case of STM, the tunneling occurs between a sharp metal tip and a conducting sample rather than molecular donor/acceptor pairs [6–10]. The tunneling current that flows between the tip and sample varies exponentially with the tip-sample distances, and typically decreases 10-fold for an angstrom increase in separation. This strong exponential dependence of the tunneling current enables STM to image directly with atomic resolution. Herein, we report STM studies of the local structure of lead-substituted Bi₂Sr₂CuO₆ single crystals, Pb_xBi_{2-x}Sr₂CuO₆. STM data recorded as a function of lead concentration shows that this substitution systematically disorders the structure of the BiO layer in this material. Comparison of these results to diffraction measurements demonstrate that important information about the local chemistry can be lost in diffraction but not STM measurements. The general implication of these results to studies of the local crystal chemistry of materials is discussed.

2. Experimental

Single crystals of Pb_xBi_{2-x}Sr₂CuO₆ were grown from CuO-rich and/or Bi₂O₃-rich melts as described previously

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¹ Dedicated to Harry B. Gray, an extraordinary scientist, teacher and friend, on the occasion of his 60th birthday.

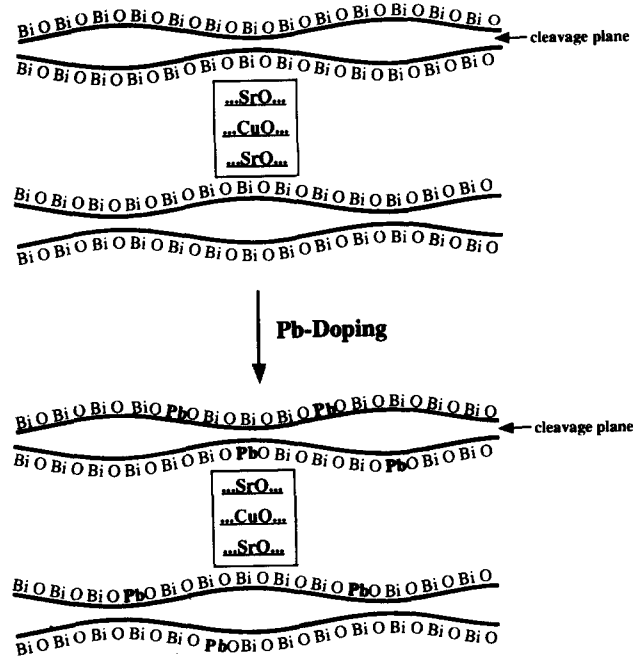


Fig. 1. Schematic illustration of Pb-substitution into the BiO layer of $\text{Bi}_2\text{Sr}_2\text{CuO}_6$.

[11,12]. The quality of the $\text{Pb}_x\text{Bi}_{2-x}\text{Sr}_2\text{CuO}_6$ crystals is affected significantly by the composition of the growth crucibles. Al_2O_3 crucibles, which have been used by many researchers, exhibit considerable reaction with the molten solid, and the crystals obtained from these crucibles have broad superconducting transitions. We have found that MgO crucibles, which do not react extensively with the molten solid, yield high-quality crystals with sharp transitions. The structure, composition, resistivity, and magnetization of the $\text{Pb}_x\text{Bi}_{2-x}\text{Sr}_2\text{CuO}_6$ crystals were carefully characterized prior to the STM studies.

The STM studies of the $\text{Pb}_x\text{Bi}_{2-x}\text{Sr}_2\text{CuO}_6$ materials were carried out in an argon-filled glove-box with a purification system that reduced the concentrations of H_2O and O_2 to below 1 ppm. The glove-box environment was used to eliminate the deleterious surface reactions that occur in ambient environment with these materials [11]. Measurements were made using a commercial STM (Nano-scope, Digital Instruments, Inc.) on cleaved crystal surfaces. The $\text{Pb}_x\text{Bi}_{2-x}\text{Sr}_2\text{CuO}_6$ crystals could be cleaved readily within the glove-box using tape, and we found that these cleaved surfaces were stable for at least 3 h. STM images were acquired in the constant current mode on at least three independent crystals for each value of $x(\text{Pb})$. The data shown in this paper are representative of the many images obtained in our investigations of these samples.

3. Results and discussion

A series three distinct $\text{Pb}_x\text{Bi}_{2-x}\text{Sr}_2\text{CuO}_6$ single crystals with $x(\text{Pb}) = 0, 0.15$ and 0.3 were investigated in

these studies. STM is ideal probe of Pb-substitution in $\text{Pb}_x\text{Bi}_{2-x}\text{Sr}_2\text{CuO}_6$ since Pb replaces Bi in the BiO layers and the Pb-doped crystals can be cleaved to expose a Bi(Pb)O layer directly at the crystal surfaces (Fig. 1). Representative STM images of the Bi(Pb)O layer of $\text{Pb}_x\text{Bi}_{2-x}\text{Sr}_2\text{CuO}_6$ crystals are shown in Fig. 2. Images of the $x(\text{Pb}) = 0$ and 0.15 samples both exhibit a one-dimensional superstructure (Fig. 2A,B). In contrast, images of samples containing higher lead concentrations do not exhibit a regular superstructure (Fig. 2C).

The average period of the superstructure in the $x(\text{Pb}) = 0$ sample is 26 \AA along the a -axis. Images acquired simultaneously with positive (empty sample electronic states) and negative bias voltages (filled sample states) show the same features. These bias voltage dependent images demonstrate that the observed superstructure corresponds to a structural feature. Bulk diffraction studies [13–15] show a similar modulation and are thus consistent with this conclusion. The underlying origin of the this structural modulation in $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ is believed to be lattice mismatch between the BiO layers and the rigid, covalently bonded CuO layer [2]. The lattice mismatch mechanism

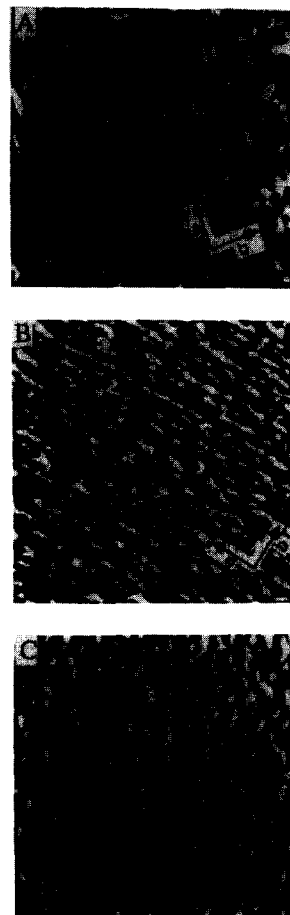


Fig. 2. $600 \text{ \AA} \times 600 \text{ \AA}$ images of (A) $\text{Bi}_2\text{Sr}_2\text{CuO}_6$, (B) $\text{Pb}_{0.15}\text{Bi}_{1.85}\text{Sr}_2\text{CuO}_6$ and (C) $\text{Pb}_{0.3}\text{Bi}_{1.7}\text{Sr}_2\text{CuO}_6$. The underlying a - b cell axes are indicated in (A) and (B).

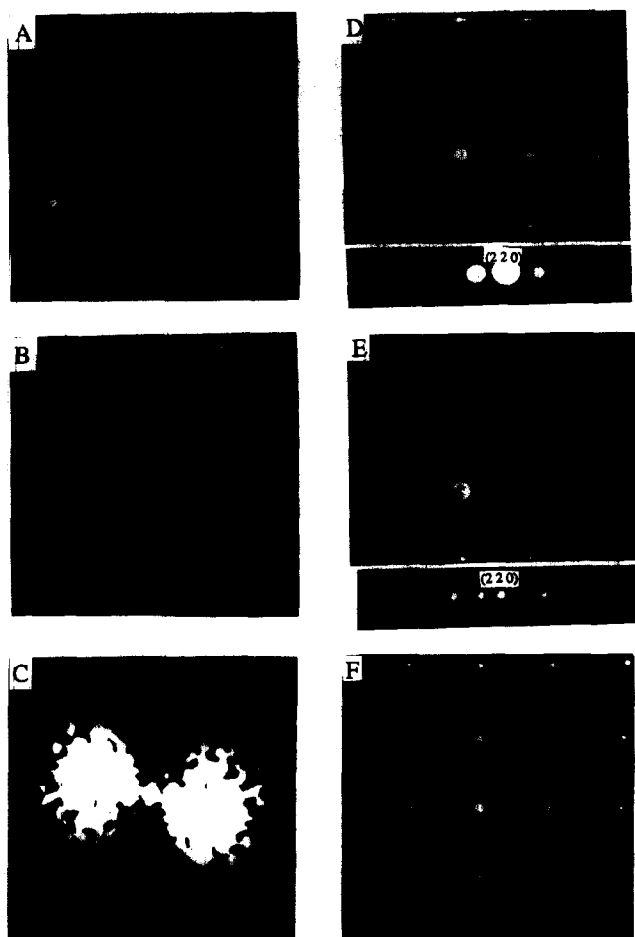


Fig. 3. (A–C) Two-dimensional Fourier transform power spectra of the STM images in Fig. 2. (D–F) electron diffraction patterns recorded at a 120 keV on the same Pb-doped samples (as used in the STM studies) with a Philips EM420 transmission electron microscope. The insets below (D) and (E) correspond to expanded views of the superlattice peaks surrounding the (220) diffraction peak.

predicts that the superstructure should be a purely sinusoidal modulation, however, our STM images demonstrate that the superstructure is not at all a sinusoidal modulation. The period varies from 22 to 27 Å. The variation in superstructure period thus suggest that this modulation is not due simply to BiO/CuO lattice mismatch but must have some substitutional doping component that causes local fluctuations in the superstructure period. In the pure samples, such doping could arise from substitution of copper ions in the BiO layer.

The importance of substitution in determining the properties of the superstructure is confirmed by the systematic structural changes that occur upon substitution of lead into the lattice. Images of $\text{Pb}_{0.15}\text{Bi}_{1.85}\text{Sr}_2\text{CuO}_6$ crystals exhibit a one-dimensional superstructure that is less regular than in $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ as evidenced by the random displacements along the *a*-axis. The distortions of the superlattice can be explained by random substitution of Pb for Bi in the Bi(Pb)O planes and the resulting differ-

ences in PbO versus BiO bonding. Significantly, distortions in the superstructure imaged directly by STM explain the decrease in correlation length reported in diffraction studies of these materials; that is, random fluctuations along the *a*-axis (due to Pb-substitution) reduce the scattering coherence. Further support of our suggestion that Pb-substitution distorts the superlattice is found in images of the $\text{Pb}_{0.3}\text{Bi}_{1.7}\text{Sr}_2\text{CuO}_6$ samples. These data exhibit a structural modulation on a 20–30 Å scale, however, this modulation is highly disordered. Because similar disorder has been observed in images of $x(\text{Pb}) = 0.3$ crystals grown under a variety of conditions, it is apparent that this disorder is representative of the intrinsic structure of these heavily doped materials. Significantly, electron diffraction measurements made on these same crystals have shown no evidence of a superstructure.

To quantify the order in these crystals and to compare the results to those obtained by electron diffraction we have used the two-dimensional structure factor $S_{2D}(\mathbf{k}) = |\rho(\mathbf{k})|^2$, where $\rho(\mathbf{k})$ is the Fourier transform of the atom density [16]. Calculations of the Fourier transform of the atom density from STM images as function of Pb concentration are shown in Fig. 3A–C. In essence, the Fourier transform of a STM image corresponds to a diffraction pattern from a very small area of a crystal, and contrasts conventional diffraction data averaged from a much larger sample volume. The Fourier transform of the STM data for $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ shows two superlattice ‘diffraction peaks’ corresponding to the superstructure wavelength of 26 Å. The electron diffraction pattern recorded on this sample is similar, and shows only a single 26 Å superlattice modulation (Fig. 3D). Several significant points are, however, seen in comparison measurements on the Pb-substituted samples. First, at intermediate Pb concentrations the comparison of $S_{2D}(\mathbf{k})$ and real-space images with in-plane electron diffraction patterns shows that the multiple superlattices inferred from electron diffraction data are due to harmonics of the principle superlattice period (Figs. 2B, 3B,E). Secondly, at higher Pb concentrations this same comparison demonstrates that the absence of a one-dimensional superstructure inferred from electron diffraction data (Fig. 3F) is due to the extreme disorder in this structural modulation.

These comparisons show clearly that local STM measurements do not obscure subtle structural variations in the $\text{Pb}_x\text{Bi}_{2-x}\text{Sr}_2\text{CuO}_6$ whereas diffraction techniques that average over a significant sample volume can lose this important information. More generally, our approach of combining real-space images with diffraction patterns calculated from the Fourier transform of these data enables a quantitative determination of local crystalline order. We believe that this approach will be generally applicable to providing detailed insight into the local chemical and structural effects of metal substitution and to enhancing the homogeneity of doping in complex inorganic materials.

Acknowledgements

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References

- [1] F.J. DiSalvo, *Science*, **247** (1992) 649.
- [2] C.M. Lieber, *Chem. Eng. News*, April 18 (1994) 28.
- [3] C.N.R. Rao and B. Raveau, *Acc. Chem. Res.*, **22** (1989) 106.
- [4] C.M. Lieber and X.L. Wu, *Acc. Chem. Res.*, **24** (1991) 170.
- [5] Z. Zhang and C.M. Lieber, *J. Phys. Chem.*, **96** (1992) 2030.
- [6] G. Binnig, H. Rohrer, C. Gerber and E. Weibel, *Phys. Rev. Lett.*, **49** (1982) 57.
- [7] R.J. Hamers, *Annu. Rev. Phys. Chem.*, **40** (1989) 531.
- [8] P. Avouris, *J. Phys. Chem.*, **94** (1990) 2246.
- [9] S.N. Magonov and M.-H. Whangbo, *Adv. Mater.*, **6** (1994) 355.
- [10] J.A. Stroscio and W.J. Kaiser (eds.), *Scanning Tunneling Microscopy*, Academic Press, New York, 1993.
- [11] X.L. Wu, Z. Zhang, Y. Wang and C.M. Lieber, *Science*, **248** (1990) 1211.
- [12] Y. Li, J. Liu and C.M. Lieber, *Phys. Rev. B*, **49** (1994) 6234.
- [13] M.A. Subramanian, C.C. Torardi, J.C. Calabrese, J. Gopalakrishnan, K.J. Morrissey, T.R. Askew, R.B. Flippen, U. Chowdhry and A.W. Sleight, *Science*, **239** (1988) 1015.
- [14] Y. Gao, P. Lee, P. Coppens, M.A. Subramanian and A.W. Sleight, *Science*, **241** (1988) 954.
- [15] O. Eibl, *Physica C*, **175** (1991) 419.
- [16] H. Dai and C.M. Lieber, *Annu. Rev. Phys. Chem.*, **44** (1993) 237.